Ionic conductivity of β-AgI

R. J. Cava and E. A. Rietman

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

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We have measured the silver-ion conductivity in single-crystal β-AgI between 330 K and the β-to-α transition at 420 K by the complex impedance method. The conductivity is approximately isotropic, with pronounced curvature in the $\log_{10}(\sigma T)$ versus $1/T$ representation. We found the surface conduction perpendicular to c to be significant. Detailed measurements in the vicinity of the β-to-α transition show no evidence for unusual pretransition silver sublattice melting.

Silver iodide has been of interest as a model compound for the study of fast-ion transport in solids since the discovery of anomalously large silver-ion conductivity in the α phase in 1914 (Ref. 1) and the intriguing proposal in 1934 of the existence of a molten silver sublattice[2] based on crude x-ray diffraction measurements. Structural models, and measurement and theoretical interpretation of the properties of the α phase, have become sophisticated in recent years. Nevertheless, recent measurements have raised new questions or reopened old ones, such as the possible existence of an order-disorder transition in the α phase.[3]

We report here new measurements of the temperature dependence of the conductivity of the low-temperature β phase of AgI, the thermodynamically stable phase from low temperatures to 420 K, the first-order β-to-α transition. The silver-ion conductivity increases by about four orders of magnitude at the phase transition. Although the basic structure of β-AgI is well established (wurtzite-type structure, hexagonal closest packing of iodine atoms with tetrahedrally coordinated silver atoms whose coordination tetrahedra share only corners), the details of the structure are not well established. Early structural studies suggested[4] a normal wurtzite-type structure at low temperature but that silver ions were slightly displaced from the centers of their coordination tetrahedra at room temperature. Later x-ray and neutron-diffraction studies[5,6] failed to confirm this type of disorder. Nonetheless, there are difficulties in the fit of the data to the normal wurtzite structural model, and the detailed structure must still be considered unresolved.[6]

Silver-ion disorder in β-AgI has been inferred from many measurements, and has been invoked in theoretical models for the β-to-α phase transition.[7-10] The specific heat, for example, is larger between 325 and 420 K than the values extrapolated from lower temperature[11,12] and has been attributed to the formation of Frenkel defects: the movement of Ag ions into normally vacant interstitial sites [0.1% (Ref. 11) and 1.0% (Ref. 12) at 419° K], or to Frenkel defects plus increased anharmonicity[13] of lattice vibrations. Due to such anharmonicities, interpretation of excess heat capacity solely in terms of Frenkel defects is ambiguous. A low-frequency dispersionless phonon mode has been identified as being favorable for the formation of Frenkel defects,[9] and the small negative thermal expan-

sion coefficient of β-AgI has also been attributed to the formation of such defects.[14]

Recent Raman scattering measurements have been the most detailed of the apparent disorder in β-AgI.[3,15] The extra features which appear in the Raman spectra at temperatures higher than 50 K are due to the relaxation of the wave-vector conservation rule, and indicate the appearance of structural disorder. The temperature dependence of the intensities of the extra spectral features is characteristic of a thermally activated partial structural disorder, attributed to the formation of Frenkel defects in the silver sublattice. Further, a dramatic change in the line shape and width of a low-energy optic mode has been observed to occur beginning at approximately 40 K below the β→α phase transition,[16] and has been attributed to the phonon-assisted activation of Frenkel defects. Measurements of the nuclear spin-lattice relaxation time of ^{127}I in β-AgI have found an anomalous increase in the relaxation rate beginning 5 K below the β→α transition temperature,[17] which has been attributed to a sharp, discontinuous increase in the concentration of diffusing silver ions, in a pretransitional silver sublattice melting. Such a discontinuous increase in the number of mobile ions would result in a significant increase in the conductivity of the β phase just below the transition.

There have been many measurements of the conductivity of β-AgI. The existence of the metastable γ phase, however, complicates the interpretation of some of the measurements made on polycrystalline samples formed either by pressing pellets of the β phase, or by cooling a polycrystalline ingot from the melt.[18,19] The γ phase, which is of the sphalerite type, forms if pellet compaction pressure exceeds 1500 psi, or in differing proportions in samples prepared from molten AgI depending on the cooling rate.[20] The difficulties in measurement of polycrystalline samples can be avoided if careful sample preparation and monitoring of phases present through x-ray diffraction is employed.[21] Three single-crystal studies on β-AgI have been reported, but the results are not in agreement. The earliest[22] found plots of $\log_{10}(\sigma T)$ versus $1000/T$ to display continuous curvature between 290 and 420 K both parallel and perpendicular to the c axis (σ is the same for all directions perpendicular to c in hexagonal symmetry crystals). Such curvature is not expected in the normal analysis of conductivity as a thermally activated

Arrhenius process. The conductivity was attributed to the motion of silver Frenkel defects. Two later studies[23,24] did not confirm the presence of curvature in $\log_{10}(\sigma T)$ against $1000/T$ plots. Both find the presence of knees in such representations at low temperature which were interpreted in the conventional sense as being due to impurities. In both studies, the energy of formation of silver interstitials and vacancies and their respective mobilities were determined. In several studies aimed primarily at determination of the pressure dependence of the conductivity,[25,26] curvature in Arrhenius plots has been observed without elaboration, as it has been in a similar study on a polycrystalline sample.[27] The interpretation of all of the conductivity measurements has been couched in the formalism of conventional Frenkel defect formation: a thermally generated silver interstitial ion and the vacant normal lattice site it leaves behind are both diffusing species. This is based on similar interpretations for conduction in AgCl and AgBr, where Frenkel defects on the order of 1.5% of the total silver population apparently occur near the melting points.[28] None of the published studies have concentrated on the behavior of the conductivity of β-AgI in the neighborhood of the β-to-α transition, and thus there has not been a test of the proposal that there is a sharp discontinuous increase in the number of mobile ions about 5 K below the phase transition. Such a conductivity anomaly may be inferred, however, from the published results of several of the studies on polycrystalline samples.[18,27,29] One purpose of the present study is to look carefully at the conductivity of β-AgI in the vicinity of the phase transition.

EXPERIMENTAL

Single crystals of β-AgI were grown at ambient temperature by the slow dilution, with distilled water, of a 4-M aqueous KI solution saturated with AgI (approximately 1.7 moles AgI/liter). Crystals were grown and stored in darkness to prevent decomposition via internal precipitation of silver. Crystals of two habits were employed: Flat hexagonal platelets for the measurements parallel to c, and small hexagonal prisms for the measurements perpendicular to c. Crystals from these growths are of the $2H$ polytype, as determined by single-crystal x-ray diffraction. Sample dimensions were such that typical electrode areas were approximately 3 and 10 mm^2 for measurements perpendicular and parallel to c, respectively, with sample thicknesses of approximately 1 mm. Silver-paint electrodes were applied to optically high-quality crystals free from voids or striations.

The experiments were designed to eliminate several difficulties that might have occurred in the former single-crystal measurements. The complex impedance of the samples was measured between 5 Hz and 13 MHz at 131 frequencies for each temperature (Hewlett-Packard 4192A meter). The sample resistance was then determined by the extrapolation to zero imaginary part of the electrode characteristic in a plot of the data in the impedance plane. The data for all temperatures and for both crystal orientations indicated that silver-paint electrodes are not generally reversible and that therefore dc or low-frequency measurements are subject to distortion by polarization effects. One of the earlier studies "conditioned" the electrodes by passage of large currents and measurement at high potential. Such conditioning can result in the decomposition of the AgI. Our impedance measurements were made at an applied potential of 1 V to eliminate possible decomposition. Inspection of the crystals after each experiment found them to be free of the fine silver precipitates that accompany such decomposition. The resistances of the samples measured were between approximately 10^3 and 10^7 Ω.

In one of the earlier single-crystal studies,[24] the conductivity perpendicular to c was found to be sensitive to the atmosphere in which the measurement was performed. This was interpreted as indicating the presence of a significant contribution by surface conduction. To determine whether surface conduction was present we performed the conductivity measurements (in both directions) on crystals with and without surface conduction guards. The guards were made by coating the entire surface of the crystals with nonconducting epoxy (excluding the regions with electrodes) which was stable to temperatures much higher than 420 K, the maximum temperature of our measurement.

Due to the martensitic nature of the β-to-α phase transition in AgI, conductivity measurements in the vicinity of the transition are greatly influenced by the presence of thermal gradients in the sample. Through optical examination of AgI crystals as they undergo the phase transition, we have observed the $\beta-\alpha$ interface (marked by a yellow-orange color difference) to move in a jerky, irregular fashion, characteristic of a transition with large associated strain and volume change. In many cases the crystals are partially transformed at a particular "temperature" and will remain so unless further energy is supplied. To determine whether earlier measurements of large increases in σ within a few degrees of the phase transition were due to the fact that the samples were actually partially transformed $\beta+\alpha$ mixtures, our samples were mounted in direct contact with large brass blocks, of total volume approximately 5×10^2 that of the crystals. This large thermal mass of brass assured both uniform sample temperature, and a large heat reservoir to drive the phase transition to completion once it began to occur.

Two distinct sets of temperature-dependent conductivity experiments were performed. In the first, impedances parallel and perpendicular to c were measured at 1°–2° increments in the range 325–420 K, to specify the general behavior of the conductivity. For temperatures less than approximately 325 K, sample impedances were too large to measure with our technique. All measurements were made on heating samples in a dry nitrogen atmosphere at a rate of 2°/h. Because the phase transition involves a large volume change, crystals shatter after being heated above 420 K—therefore all measurements were made on different crystals from the same growth batch. In the second set of measurements, designed to measure the conductivity in the vicinity of the phase transition, impedances were measured in 0.05 to 0.2 K temperature intervals between 413 and 420 K, through the β-to-α phase transition. Samples were heated at the same rate for both

sets of measurements, and all measurements were performed on a minimum of three different crystals to verify the reproducibility of the results.

RESULTS

Complex impedance measurements for all samples were consistent with model circuits[30] representing the sample/electrode system as parallel sample resistance and capacitance, in series with a Warburg-type impedance representing the electrode characteristic. The arcs in the standard plots of imaginary-versus-real part of the impedance were slightly depressed semicircles for high frequencies (bulk conductivity response) with a straight-line behavior (electrode characteristic) at low frequencies, with a slope approximately equal to 1. The sample resistance was taken at the intersection of the bulk response arc with the real axis. An example of the data is presented in Fig. 1.

The results of the experiments on the measurement of conductivities between 325 and 420 K are presented in Fig. 2 [$\log_{10}(\sigma T)$ versus $1000/T$] and Fig. 3 ($\log_{10}\sigma$ versus $1000/T$). For both representations, the data show curvature over the whole temperature range. Comparison of the conductivity measured with and without the surface conduction guard indicates that surface conduction dominates the measured conductivity perpendicular to c at low temperatures, and is insignificant in the c direction for all temperatures (Fig. 2). The bulk conductivity of β-AgI is very nearly isotropic between 330 and 420 K, with the c-axis conductivity only slightly smaller (by approximately 15% at 370 K). The magnitudes ($\sim 4.5 \times 10^{-4}$ Scm^{-1}) and activation energies (~ 1.0 eV) of the conductivity are approximately equivalent for both directions at 420 K. The activation energies for conduction increase from approximately 0.6 to 1.0 eV between 330 and 420 K.

The results of the detailed conductivity measurements in the vicinity of the β-to-α phase transition are presented in Fig. 4. Within the accuracy of the measurements, the conductivities parallel and perpendicular to c are equal in magnitude for the 7 K just before the transition. The data parallel to c fall on a straight line of slope 1.05 eV. The data for conductivity perpendicular to c follow a straight line of slope 0.99 eV with a small positive deviation beginning about 1 K below the phase transition. The observed
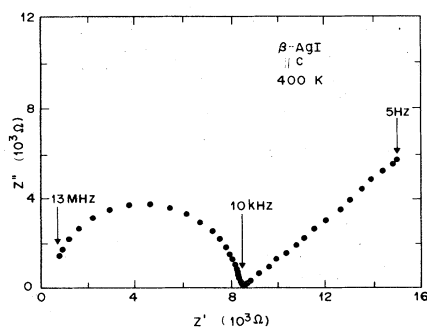

FIG. 1. Complex impedance of a β-AgI single crystal measured parallel to c at 400 K. Every other data point has been omitted for clarity.
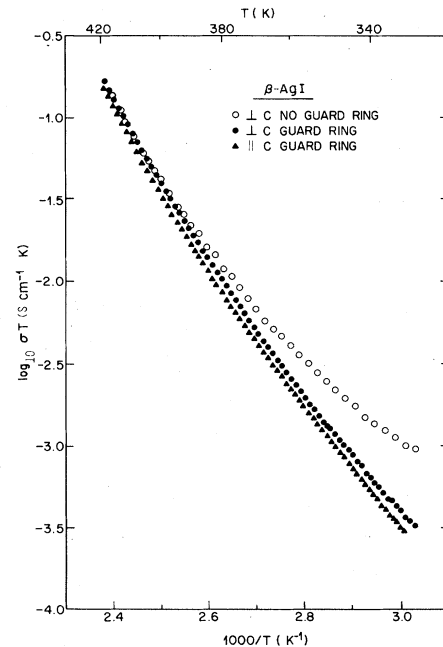

FIG. 2. Conductivity temperature product of β-AgI single crystals between 330 and 420 K. Contribution of surface conduction is large perpendicular to c but is negligible, and therefore not shown, for the direction parallel to c.

conductivity perpendicular to c at 420.3 K is about 5% higher than that extrapolated from the straight line between 413 and 419 K. The values of the conductivity are in excellent agreement with the extrapolation of the conductivities obtained between 330–420 K. We see no indication of an unusual increase in conductivity in the vicini-
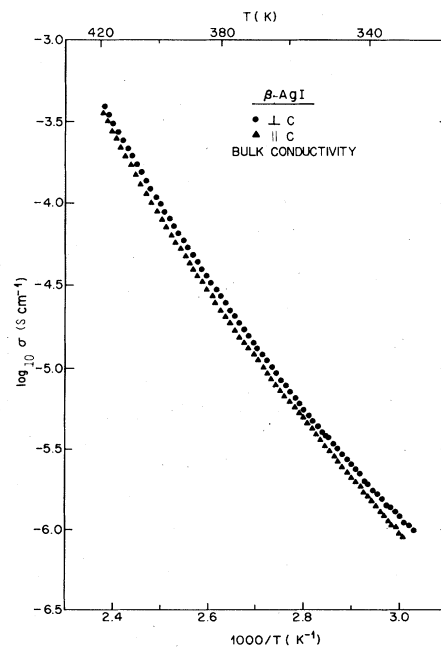

FIG. 3. Bulk conductivity of β-AgI single crystals parallel and perpendicular to c, surface guarded samples only.
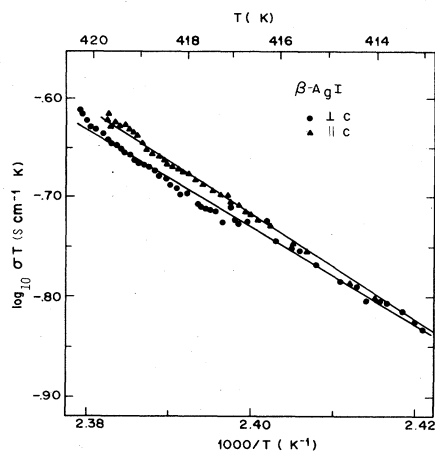
FIG. 4. Conductivity temperature product of β-AgI single crystals parallel and perpendicular to c, in the vicinity of the β-to-α phase transition.

ty of the phase transition. The β-to-α phase transition consistently occurred approximately 0.5° higher for samples whose conductivity was measured perpendicular to c. This superheating of the β phase is due to the fact that the c axis is not in direct contact with the heat source, and a small amount of extra driving force is needed to nucleate the transition, which propagates parallel to c.

CONCLUSIONS AND DISCUSSION

We have found the conductivity of β-AgI to be essentially isotropic between 325 K and the β-to-α phase transition. This implies that fast diffusion pathways must exist for diffusion perpendicular to c with comparable silver-ion mobility to that in the crystallographic tunnel of face-shared octahedral sites running parallel to c. In the temperature range studied, conductivity increases from approximately 10^{-6} to 4.5×10^{-4} Scm^{-1}, and the activation energy increases from approximately 0.6 to 1.0 eV. When plotted in the $\log_{10}(\sigma T)$ versus $1000/T$ representation, curvature is observed over the whole temperature range of the experiment. The curvature is the same for all crystals measured, whose linear dimensions varied by approximately a factor of 3. Surface conduction contributes significantly to the total conductivity perpendicular to c at low temperatures. This may be due to either the difference in geometries of the crystals employed in the measurements in different directions, or a true anisotropy in surface conduction. The results for conductivity parallel and perpendicular to c in the absence of surface conduction guards are identical to one set of single-crystal data previously published.[22] The two other single-crystal measurements concentrated on a temperature range lower than that studied here. The magnitudes of the bulk conductivities we find at 333 K are in excellent agreement with one of those studies,[23] as is our observed activation energy perpendicular to c. Neither lower temperature study found curvature in the $\log_{10}(\sigma T)$ versus $1000/T$ representation of the conductivity. In light of the current results it would be of interest to determine whether the curvature first appears at approximately 50 K, as suggest-

ed by the Raman scattering studies. Comparison to conductivity studies performed on AgI powers[18,19,21] indicates single-crystal and powder results to be in good agreement at high temperatures but that powder conductivity is higher than that of single crystals for temperatures below approximately 380 K. This suggests that grain boundaries may provide a high diffusivity path for Ag at low temperatures. Earlier studies of the conductivity of β-AgI have been interpreted in terms of a classical Frenkel defect model.[22-24] This model in the strict sense cannot apply to β-AgI. It dictates that a silver ion leaves its normal lattice site, entering a normally unoccupied sublattice on which it diffuses, with the vacancy left behind *also* diffusing, on the normally occupied sublattice. Migration energies for vacancies and interstitials have been determined from conductivity data for β-AgI.[23,24] Although the Frenkel defect model works well for AgBr and AgCl, rocksalt-structure compounds where silver coordination octahedra share edges with each other (allowing exchange of a vacancy and an Ag ion), and faces with the normally vacant tetrahedral interstitial positions, it is not applicable to diffusion in β-AgI due to two factors. Firstly, vacancy diffusion on the normally occupied sublattice cannot occur: The silver-ion tetrahedra share only corners and therefore diffusion of a vacancy in the occupied sublattice requires exchange of a vacancy and a filled position via a jump of a silver ion directly through an iodine ion. The exchange of a vacancy and an ion on the normally occupied sublattice must be mediated through an interstitial ion. Secondly, the β-AgI structure contains chains of normally vacant octahedral sites sharing faces, running parallel to c, resulting in a fast diffusion channel not present in rocksalt-type compounds, and implying the domination of interstitial motion similar to that found in α-AgI—type compounds.

The formation of an interstitial ion from a normally occupied site is nonetheless important for β-AgI, as Ag conductivity at the magnitudes observed cannot occur without the presence of interstitial ions. Such interstitial diffusion can be represented by the expressions

$$\sigma_i = ne\mu_i = \frac{A}{T} \exp(-E_F/kT) \exp(-U_i/kT) ,$$

where n is the concentration of interstitial ions and μ_i is their mobility. Subscripts refer to the crystallographic a and c directions, and A contains information on geometry and attempt frequency of the conductivity jumps. The concentration of interstitial ions is proportional to $\exp(-E_F/kT)$. In this model, E_F is independent of direction.[24] The quantities U_a and U_c are the energy of migration of the interstitial in the a and c directions. These expressions yield straight lines in $\log_{10}(\sigma T)$ versus $1000/T$ plots, which would have different slopes along a and c depending solely on the differences between U_a and U_c, and have been used in earlier studies to interpret the conductivity of β-AgI. This model can also be employed to account for the curvature in $\log_{10}(\sigma T)$ versus $1000/T$ plots by postulating a temperature dependence of E_F and/or U_i. A temperature-dependent Frenkel defect formation energy has been much discussed for AgBr and AgCl in this context.[28,31-33] This may well be an explanation for

the curvature in the $\log_{10}(\sigma T)$ versus $1000/T$ plots we have observed for β-AgI. The large "excess" conductivity [in excess of that extrapolated from the slope of $\log_{10}(\sigma T)$ versus $1000/T$ at temperatures less than 360 K] at high temperature in β-AgI would require a decrease in the free energy required to form an interstitial defect significantly larger than the 0.2 eV estimated for AgBr near its melting point[32,33] and would require a significant softening of the lattice, as has been observed in AgBr and AgCl.[31] Although the β-AgI lattice is soft, neutron scattering,[13] elastic constant,[34] and thermal expansion[14] measurements have not to this date indicated an unusual softening of the β phase as it approaches the phase transition. The curvature we have observed in β-AgI is many times larger than those observed in AgBr and AgCl. Inspection of Fig. 2 suggests that the curvature can be described by a simple expansion of the usual Arrhenius expression for the conductivity: $\sigma=(A/T)\exp[-E_a(T)/kT]$, where both interstitial formation and migration energy are included in $E_a(T)$. The temperature dependence of $E_a(T)$ is well described by the simple expression: $E_a(T)=B+C/T$, where for Arrhenius behavior $C=0$. The parameters for the fits of this expression to the conductivity data are presented in Table I and are seen to be approximately equivalent for both directions. The data are described to within a fraction of a percent in both directions, consistent with a simple (but strong) temperature dependence of interstitial defect formation or migration energies.

We would like to suggest an alternative explanation for the observed curvature in the $\log_{10}(\sigma T)$ versus $1000/T$ plots for β-AgI, based primarily on the availability of two different sets of interstitial sites for the diffusing silver ion. Table II presents selected interatomic distances in β-AgI. The normally occupied silver positions are nearly perfectly tetrahedral in geometry, and share only corners with each other. Every occupied tetrahedron shares a face with a vacant tetrahedron of identical geometry. The shared face is in the basal plane, and thus filled and vacant tetrahedral sites occur in pairs with the line connect-

ing their centers parallel to c. A silver ion occupying the normally vacant tetrahedral site would have ideal Ag-I separations (Table II). These sites share three edges (with a large Ag-Ag separation) with filled tetrahedral sites, as well as the face with the normally occupied site in the pair. The short face-shared Ag-Ag distance (Table II) indicates that the vacant tetrahedral site is likely to be occupied only if the near-neighbor normally occupied site is empty. The vacant octahedral interstices share triangular faces with each other to form one-dimensional tunnels parallel to c. The Ag-I separation in this site is large, 3.25 Å, and probably quite unfavorable. [The octahedrally coordinate Ag-I separation in NaCl-type AgI is 2.91 Å (Ref. 35).] The interstitial ion may, however, be displaced from the center of the octahedron to shorten some of the Ag-I distances. Considering the possible Ag-Ag separations, an interstitial octahedral site can be occupied regardless of the empty/filled status of nearby normally occupied tetrahedral sites.

Silver-ion jumps in β-AgI are likely to occur through shared triangular faces (saddle points), by direct analogy to α-AgI, where the primary diffusion process is through the shared triangular face between neighboring tetrahedral sites.[6,36] In α-AgI this face is slightly distorted, with an average Ag-I separation of 2.64 Å. In β-AgI the triangular faces are of two types—those in the basal plane and those through which jumps roughly parallel to the basal plane occur. Due to the nearly ideal geometry of the β-AgI wurtzite structure, a diffusing Ag ion has 3 I neighbors at 2.66 Å for jumps through the centers of both types of face, comparable to the distances in the α phase. For a jump through a shared edge in β-AgI, an unfavorable two-coordinate Ag-I geometry is required (Ag-I separation of 2.3 Å), and jumps through shared corners are prohibited as they would be through an iodine ion. A lattice net of possible diffusion pathways for β-AgI can be constructed based on interstitial occupancy of both tetrahedral and octahedral vacant sites, and diffusive jumps through triangular polyhedron faces. The result

TABLE I. Parameters describing fits to the conductivity data for β-AgI.

$$\sigma=\frac{A}{T}\exp[-E_a(T)/kT] \quad \text{where} \quad E_a(T)=B+\frac{C}{T}$$

Parameter	Perpendicular to C	Parallel to C
A (Scm^{-1} K)	1.24×10^{22}	7.36×10^{21}
B (eV)	2.76	2.73
C (eVK)	-357	-350
R (%)	0.18	0.42

$$\sigma=\frac{A}{T}\exp(-E_1/kT)+\frac{B}{T}\exp(-E_2/kT)$$

Parameter	Perpendicular to C	Parallel to C
A (Scm^{-1}K)	1.2×10^{15}	1.2×10^{15}
E_1 (eV)	1.34	1.34
B (Scm^{-1}K)	1.0×10^7	1.0×10^7
E_2 (eV)	0.69	0.69
R (%)	0.40	0.54

$$R=\frac{\sum|\ln(\sigma T)_{\text{OBS}}-\ln(\sigma T)_{\text{calc}}|}{\sum\ln(\sigma T)_{\text{obs}}}$$

TABLE II. Selected interatomic distances for β-AgI, for occupied and interstitial positions.[a]

Site	Ag-I separation		Type of sharing	To normally occupied site		
	Number	Distance (Å)		Ag-Ag separation		
				Number	Distance (Å)	
Normal	3	2.82	Corners	12	4.60	
tetrahedral	1	2.80				
Vacant	3	2.82	Faces	1	1.93	
tetrahedra	1	2.80	Edges	3	3.01	
Vacant	6	3.25	Faces	3	2.81	
octahedral			Edges	3	3.89	
Saddle point	3	2.67				

[a]Based on the β-AgI structure (Ref. 6): $P6_3mc, a_0 = 4.599$, $c_0 = 7.520$. Positions $(\frac{1}{2}, \frac{2}{3}, z)$: $z = 0.0$, Iodine; $z = 0.628$ occupied Silver tetrahedral site; $z = 0.372$, vacant tetrahedral site; position $(0,0,z):z = \frac{1}{4}$, vacant octahedral site.

projected into the hexagonal basal plane is presented in Fig. 5. Normally occupied tetrahedral sites, vacant tetrahedral sites, and vacant octahedral sites are represented by T, V, and O, respectively, and allowed diffusion paths are represented by solid lines. The diffusion paths can be presented conveniently projected into planes perpendicular to c with elevations near $z = 0.25$ and $z = 0.75$. The configuration of pathways on successive planes is identical, but T and V sites alternate along c, whereas O sites form infinite chains in that direction. Diffusive jumps along c occur between O sites in the chain $1/2c$ apart, or by jumps between T and V sites sharing faces. T-V type jumps do not form infinite chains parallel to c but are interrupted after only one jump by an iodine ion.

Inspection of Fig. 5 indicates that silver-ion diffusion cannot occur either parallel or perpendicular to c without motion through an octahedral interstice. Occupancy of the normally vacant tetrahedral site is not essential to conductivity, but consideration of its near-neighbor atoms indicates it to have a lower or at least comparable energy to the octahedral interstice, and that it is therefore likely to contribute to the conduction process. Because the ener-
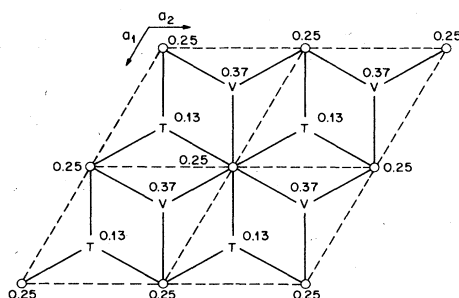

FIG. 5. Configuration of silver sites near $Z = 0.25$ in β-AgI projected into a plane perpendicular to c. Diffusive pathways are shown as solid lines. Normally occupied tetrahedral sites, octahedral interstitial sites, and normally vacant tetrahedral sites are represented by T, O, and V, respectively. Fractional coordinates of each site along c are also shown. The configuration of pathways on successive planes is identical, but T and V sites alternate along c, whereas O sites form infinite chains in that direction. Dashed lines indicate unit-cell boundaries.

gies of the tetrahedrally coordinates and octahedrally coordinated interstitial sites are different, the ratio of the contribution to the conductivity of processes involving the two types of sites will depend on temperature. The total conductivity will be due to the sum of many parallel processes made up of elementary diffusive steps in series. The probability of occurrence of a particular diffusive step depends on the difference in energy between the site occupied and the diffusion saddle point by $p_i \propto \exp -[(E_{SP} - E_i)/kT]$, where E_i is the energy of the site (T, V, or O) and E_{SP} is the energy of the saddle point. The ratio of the probabilities of the elementary steps is therefore significantly dependent on temperature. The resultant temperature-dependent summing of parallel processes would result in curvature in the $\log_{10}(\sigma T)$ versus $1000/T$ plots for both crystallographic directions, as observed. To test the possible validity of this hypothesis we have fit an expression for two parallel Arrhenius-type conductivity processes to the conductivity data. The expression is of the form

$$\sigma = (A/T)\exp(-E_1/kT) + (B/T)\exp(-E_2/kT) ,$$

where E_1 and E_2 are the activation energies for the two processes. The parameters for the fits are presented in Table I: The expression describes the conductivity data in both directions to within a fraction of a percent, and within the error the parameters are equivalent in both directions. The process with low activation-energy (0.69 eV) dominates in the low-temperature region, with the higher-activation-energy process (1.34 eV) dominating the observed conductivity at temperatures greater than approximately 410 K. Thus the observed curvature in $\log_{10}(\sigma T)$ versus $1000/T$ in β-AgI is equally well described by a model of temperature-dependent interstitial formation or migration energy, or a model of temperature-dependent summing of parallel conductivity processes. A precise microscopic probe, which would distinguish interstitial octahedral from interstitial tetrahedral silver ions, might allow the determination of a unique conduction mechanism.

Although the characteristics of the conductivity require interstitial silver-diffusion processes, we unfortunately

cannot estimate the fraction of silver ions which occupy interstitial sites. An upper bound of several percent is indicated by heat capacity and neutron-diffraction measurements. Molecular dynamics calculations similar to those performed on α-AgI would be of interest in the further elucidation of the conduction process in β-AgI, as would careful single-crystal diffusion measurements. Finally, we have not observed a significant increase in conductivity in the near vicinity of the β-to-α phase transition. This suggests that the change in the local environment of the iodine ions observed in NMR experiments within 5° of the transition may be due to a process other than the discontinuous pretransition increase in the number of mobile silver ions originally proposed, perhaps an increased disorder which does not contribute significantly to long-range silver motion.

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